Supplementary Information

Proton transfer anionic polymerization with C–H bonds as dormant species

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Synthesis of cumyl isobutyrate (2). Cumyl isobutyrate (**2**) was synthesized via a reaction between isobutyric anhydride and 2-phenyl-2-propanol. Isobutyric anhydride (7.37 mL, 44.3 mmol) was added to a mixture of 2-phenyl-2-propanol (5.48 g, 40.2 mmol) and DMAP (51.9 mg, 0.425 mmol). After stirring at 100 °C for 23 h, the reaction was quenched by cooling the solution to 0 °C. The quenched solution was diluted with Et_2O and washed with a saturated aqueous Na_2CO_3 solution and distilled water. The solvent was removed by evaporation to give the crude product. After purification by column chromatography on silica gel with *n*-hexane/Et_2O (95/5) as the eluent, **2** was obtained as a pale-yellow solid (5.34 g, 25.9 mmol, 64% yield). ^1H NMR ($CDCl_3$, r.t.): δ 1.15 (d, 6H, $(CH_3)_2CH$, J = 6.9 Hz), 1.76 (s, 6H, $OC(CH_3)_2C_6H_5$), 2.53 (sept, 1H, $(CH_3)_2CH$, J = 6.9 Hz), and 7.20–7.38 (m, 5H, C_6H_5) (fig. S23A). ^{13}C NMR ($CDCl_3$, r.t.): δ 19.00 ($(CH_3)_2CH$), 28.60 ($OC(CH_3)_2C_6H_5$), 34.80 ($(CH_3)_2CH$), 80.90 ($OC(CH_3)_2C_6H_5$), 124.1 (Ar-*C*2), 126.9 (Ar-*C*4), 128.2 (Ar-*C*3), 146.1 (Ar-*C*1), and 175.6 (*C*(O)O) (fig. S23B).

Synthesis of vinyloxyethyl isobutyrate (5). Vinyloxyethyl isobutyrate (**5**) was synthesized via a reaction between isobutyryl chloride and ethylene glycol monovinyl ether. Isobutyryl chloride (10.0 mL, 100 mmol) was added dropwise to a mixture of ethylene glycol monovinyl ether (9.20 mL, 95.2 mmol), triethyl amine (13.8 mL, 100 mmol), and THF (30 mL) at 0 °C. The reaction mixture was gradually warmed to 20 °C. After stirring for 4 h, the reaction was quenched by cooling the solution to 0 °C. The quenched solution was diluted with Et_2O and washed with distilled water. The solvent was removed by evaporation to give the crude product. After purification by distillation (175 Pa, 126 °C), **5** was obtained as a colorless liquid (4.76 g, 30.0 mmol, 32% yield). ^1H NMR ($CDCl_3$, r.t.): δ1.18 (d, 6H, $(CH_3)_2CH$-, J = 6.8 Hz), 2.59 (sept, 1H, $(CH_3)_2CH$-, J = 6.8 Hz), 3.89 (t, 2H, $CH_2{=}CHOCH_2$, J = 4.6 Hz), 4.04 (dd, 1H, $CH_2{=}CH$, J_{gem} = 2.4 Hz and J_{vic} = 6.8 Hz), 4.21 (dd, 1H, $CH_2{=}CH$, J_{gem} = 2.4 Hz and J_{vic} = 14.4 Hz), 4.31 (t, 2H, $CH_2OC(O)C(CH_3)_2$, J = 4.8 Hz), and 6.48 (dd, 1H, $CH_2{=}CH$, J = 6.8 Hz J = 14.4 Hz) (fig. S24A). ^{13}C NMR ($CDCl_3$, r.t.) δ: 18.97 ($CHCH_3$), 33.85 ($CH(CH_3)_2$), 62.50 ($C(O)OCH_2$), 65.83 ($C{=}CHOCH_2$-), 86.94 ($CH_2{=}CH$), 151.5 ($CH_2{=}CH$), and 177.1 ($C{=}O$) (fig. S24B).

Synthesis of 2-(*tert*-butyldimethylsiloxy)ethyl isobutyrate (6). 2-(*tert*-Butyldimethylsiloxy)ethyl isobutyrate (**6**) was synthesized by the following procedure. 2-Hydroxyethyl isobutyrate was first synthesized by a reaction between isobutyric acid and ethylene glycol. H_2SO_4 (1.00 mL, 18.7 mmol) was added to the mixture of isobutyric acid (10.5 mL, 112 mmol) and ethylene glycol (62 mL, 1.12 mol). The reaction mixture was heated to 80 °C. After 4 h, the reaction was quenched by cooling the solution to room temperature. The solution was diluted with CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 solution and distilled water. The solvent was removed by evaporation to give crude 2-hydroxyethyl isobutyrate (6.95 g, 52.6 mmol, 47% yield). Then, the hydroxy group was protected with *tert*-butyldimethylsilyl chloride. Crude 2-hydroxyethyl isobutyrate (6.95 g, 52.6 mmol) was added dropwise to a mixture of *tert*-butyldimethylsilyl chloride (7.56 g, 50.2 mmol), triethylamine (7.60 mL, 54.8 mmol), and CH_2Cl_2 (4.0 mL) at 0 °C. The reaction mixture was gradually warmed to 20 °C. After stirring for 4 h, the product was extracted with CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 solution and distilled water. The solvent was removed by evaporation to give the crude product. After purification by column chromatography on silica gel with *n*-hexane/Et_2O (20/1) as the eluent, **6** was obtained as a colorless liquid (1.61 g, 6.53 mmol, 13% yield). ^{1}H NMR ($CDCl_3$, r.t.): δ 0.08 (s, 6H, -Si(C*H*$_3$)$_2$-), 0.9 (s, 9H, -Si(CH$_3$)$_2$C(C*H*$_3$)$_2$), 1.18 (d, 6H, (C*H*$_3$)$_2$CH-, *J* = 6.8 Hz), 2.57 (sept, 1H, (CH$_3$)$_2$C*H*-, *J* = 6.8 Hz), 3.81 (t, 2H, -COOC*H*$_2$-, *J* = 5.2 Hz), and 4.14 (t, 2H, -C*H*$_2$OSi-, *J* = 5.2 H) (fig. S25A). ^{13}C NMR ($CDCl_3$, r.t.): δ –5.31 (-Si(*C*H$_3$)$_2$), 18.34 (-Si*C*(CH$_3$)$_3$), 19.05 (-CH(*C*H$_3$)$_2$), 25.86 (-SiC(*C*H$_3$)$_3$), 34.00 (-*C*H(CH$_3$)$_2$), 61.30 (-CH$_2$OSi-), 65.58 (COO*C*H$_2$-), and 177.1 (*C*=O) (fig. S25B).

Synthesis of 1,3,5-cyclohexanetriol triisobutyrate (7). 1,3,5-Cyclohexanetriol triisobutyrate (**7**) was synthesized by a reaction between isobutyric chloride and 1,3,5-cyclohexanetriol. Isobutyryl chloride (16.0 mL, 151 mmol) was added dropwise to a mixture of 1,3,5-cyclohexanetriol (1.50 g, 11.3 mmol), DMAP (0.214 g, 1.70 mmol), pyridine (12.7 mL, 158 mmol), and 1,4-dioxane (30 mL) at 0 °C. The reaction mixture was gradually warmed to 20 °C. After stirring for 2 h, the reaction mixture was heated to 50 °C. After 20 h, the reaction was quenched by cooling the solution to room temperature. The quenched solution was diluted with $CHCl_3$ and washed with 1 N NaOH aqueous solution. The solvent was removed by evaporation to give the crude product. After purification by column chromatography on silica gel with *n*-hexane/EtOAc (9/1) as the eluent, **7** was obtained as a white solid (1.23 g, 3.59 mmol, 32% yield). ^{1}H NMR ($CDCl_3$, r.t.): δ 1.14-1.91 (m, 18H, (C*H*$_3$)$_2$CH-), 1.41-1.47, 1.52-1.62 (m, 3H, -C*H*$_{a2}$-), 2.07-2.12, 2.28-2.24 (m, 3H, -C*H*$_{e2}$-), 2.45-2.61 (m, 2H, (CH$_3$)$_2$C*H*-), 4.76-4.84, 5.06-5.13, and 5.28-5.32 (m, 3H, -OC*H*-) (fig. S26A). ^{13}C NMR ($CDCl_3$, r.t.): δ 18.92 (-CH(*C*H$_3$)$_2$), 33.97-34.08 and 34.79 (-*C*H(CH$_3$)$_2$), 36.22 (-*C*H$_2$-), 36.44 (-*C*H$_2$-), 66.62, 67.08, 67.63 (-O*C*H-), and 176.0-176.2 (*C*=O) (fig. S26B).

Synthesis of the HCl adduct of 5. The HCl adduct of **5** was synthesized by bubbling dry HCl gas through a solution of **5** in *n*-hexane. The HCl gas was generated by adding concentrated H_2SO_4 dropwise to NaCl powder and was dried by passing through concentrated H_2SO_4 and a column packed with $CaCl_2$. The dehydrated HCl gas was bubbled into a mixture of **5** (7.91 g, 50 mmol) and *n*-hexane (43 mL) at –78 °C. After HCl bubbling for 30 min, N_2 gas was bubbled for 30 min to remove the excess HCl gas. After the reaction solution was gradually warmed to 0 °C, N_2 gas was bubbled for another 30 min. Quantitative formation of the product was confirmed by ^1H NMR spectroscopy. The concentration of the product was measured by ^1H NMR spectroscopy with an *n*-hexane solution of EtOAc with a known concentration. ^1H NMR ($(CD_3)_2CO$, r.t.): δ 1.22 (d, 6H, $(CH_3)_2CHC(O)$, $J = 6.8$ Hz), 1.77 (d, 3H, CH_3CHCl, $J = 5.6$ Hz), 2.56 (sept, 1H, $(CH_3)_2CHC(O)$, $J = 6.8$ Hz), 3.72 and 4.06 (m, 2H, $OCH_2CH_2OC(O)$), 4.20 and 4.30 (m, 2H, $C(O)OCH_2CH_2O$), and 5.70 (q, 1H, $CH_3CHCl(OCH_2\text{-})$, $J = 5.6$ Hz) (fig. S27).

Supplementary Table 1. Effects of CTAs on anionic polymerization of TBMA[a]

entry	CTA	$[\mathrm{M}]_0/[\mathrm{CTA}]_0$	time	conv. (%)[b]	M_{n}(calcd)[c]	M_{n}[d]	Đ[d]
1	none	–	10 min	>99	—	55700	1.96
2	**1**	25	1 h	>99	3700	5300	1.23
3[e]	**1**	50	1 h	>99	7200	10200	1.27
4[f]	**1**	100	1 h	>99	14300	16400	1.32
5	**2**	25	2 min	99	3800	4400	1.18
6	**3**	25	1 h	>99	3800	4800	1.19
7	**4**	25	30 min	>99	3700	4700	1.25

[a]Polymerization condition: $[\mathrm{M}]_0/[\mathrm{CTA}]_0/[\mathrm{KHMDS}]_0/[\text{18-crown-6}]_0$ = 750/30/3/3.3 mM in THF at 0 °C. [b]Determined by gravimetric analysis. [c]M_{n}(calcd) = MW(TBMA) × conv. + MW(CTA). [d]Determined by SEC. [e]$[\mathrm{M}]_0/[\mathrm{CTA}]_0/[\mathrm{KHMDS}]_0/[\text{18-crown-6}]_0$ = 750/15/1.5/1.65 mM. [f]$[\mathrm{M}]_0/[\mathrm{CTA}]_0/[\mathrm{KHMDS}]_0/[\text{18-crown-6}]_0$ = 750/7.5/0.75/0.88 mM.

Supplementary Table 2. Effect of base catalysts on anionic polymerization of TBMA[a]

entry	base catalyst	additive	time	conv. (%)[b]	M_{n}(calcd)[c]	M_{n}[d]	Đ[d]
1	LiHMDS	12-crown-4	3 min	>99	3800	721400	1.67
2	NaHMDS	15-crown-5	10 min	>99	3800	59700	1.30
3	KHMDS	18-crown-6	2 min	>99	3800	4400	1.18
4	KO*t*Bu	18-crown-6	2.5 min	>99	3800	4200	1.18
5[e]	KH	18-crown-6	16 h	>99	3700	4500	1.38
6	KHMDS	none	2 min	>99	3800	4900	1.59

[a]Polymerization condition: $[\mathrm{M}]_0/[\mathbf{2}]_0/[\text{base catalyst}]_0/[\text{additive}]_0$ = 750/30/3/3.3 or 0 mM in THF at 0 °C. [b]Determined by gravimetric analysis. [c]M_{n}(calcd) = MW(TBMA) × conv. + MW(CTA). [d]Determined by SEC. [e]**4** was used in place of **2**.

Supplementary Table 3. Anionic polymerization of TBMA under various conditions[a]

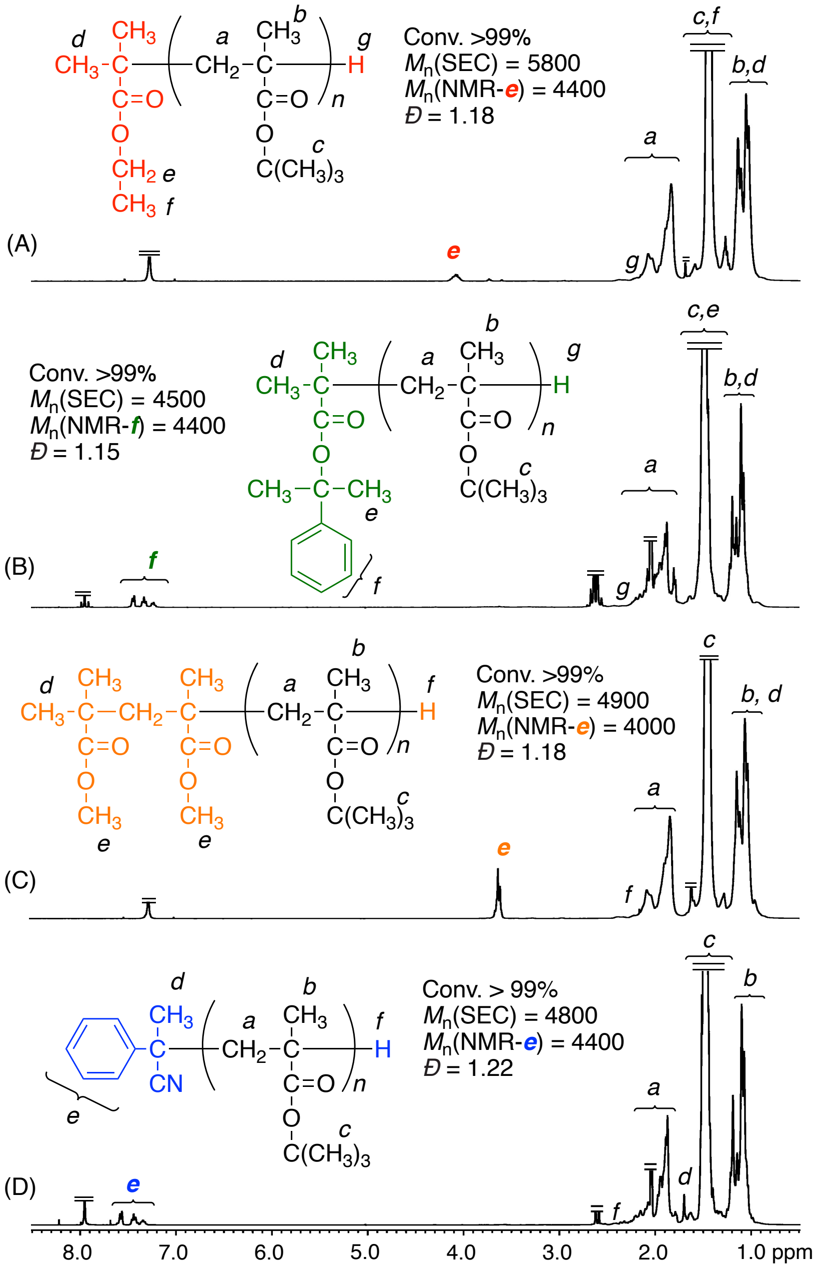
entry	solvent	temp. (°C)	$[\mathrm{M}]_0/[\mathrm{CTA}]_0$	time	conv. (%)[b]	M_{n}(calcd)[c]	M_{n}[d]	Đ[d]
1	THF	0	25	10 min	>99	3700	4500	1.13
2	toluene/THF (9/1)	0	25	10 min	>99	3700	4500	1.10
3[e]	toluene/THF (9/1)	0	10	15 min	>99	1600	2100	1.14
4[f]	toluene/THF (9/1)	0	50	1 h	>99	7200	8700	1.16
5[g]	toluene/THF (9/1)	0	100	1 h	>99	14400	15400	1.40
6	toluene/THF (9/1)	–78	25	10 min	>99	3700	4200	2.12
7	toluene/THF (9/1)	–40	25	10 min	>99	3700	4300	1.38
8	toluene/THF (9/1)	10	25	10 min	>99	3700	4200	1.12
9	toluene/THF (9/1)	20	25	1 min	>99	3700	4400	1.09

[a] Polymerization condition: $[\mathrm{M}]_0/[\mathbf{4}]_0/[\mathrm{KO}t\mathrm{Bu}]_0/[\text{18-crown-6}]_0$ = 750/30/3/3.3 mM in THF at 0 °C. [b]Determined by gravimetric analysis. [c]M_{n}(calcd) = MW(TBMA) × conv. + MW(**4**). [d]Determined by SEC. [e]$[\mathrm{M}]_0/[\mathbf{4}]_0/[\mathrm{KO}t\mathrm{Bu}]_0/[\text{18-crown-6}]_0$ = 750/75/7.5/8.25 mM. [f]$[\mathrm{M}]_0/[\mathbf{4}]_0/[\mathrm{KHMDS}]_0/[\text{18-crown-6}]_0$ = 750/15/1.5/1.65 mM. [g]$[\mathrm{M}]_0/[\mathbf{4}]_0/[\mathrm{KO}t\mathrm{Bu}]_0/[\text{18-crown-6}]_0$ = 750/7.5/0.75/0.88 mM.

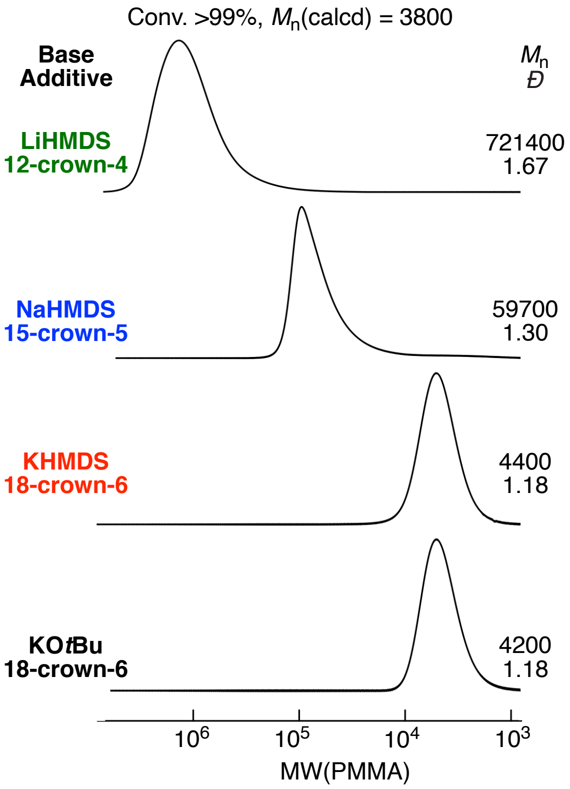
Supplementary Table 4. Effects of *t*BuOH on anionic polymerization of TBMA[a]

entry	[*t*BuOH]$_0$/[KO*t*Bu]$_0$	time	conv. (%)[b]	M_n(calcd)[c]	M_n[d]	$Đ$[d]
1	0	4 sec	86	3300	3500	1.24
2	0	2.5 min	>99	3800	4200	1.18
3	1	2 min	83	3200	3500	1.27
4	1	10 min	94	3500	3400	1.28
5	2	2 min	53	2100	2100	1.35
6	2	3 h	>99	3800	4500	1.20
7	3	2 min	19	900	1000	1.36
8	3	1 h	81	3100	3100	1.22

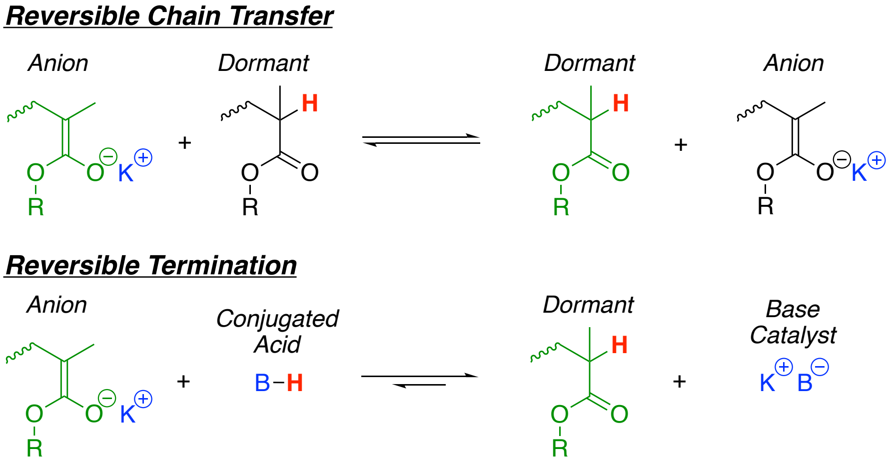
[a] Polymerization condition: [M]$_0$/[**2**]$_0$/[KO*t*Bu]$_0$/[18-crown-6]$_0$/[*t*-BuOH]$_0$ =750/30/3.0/3.3/0-9.0 mM in THF at 0 °C. [b] Determined by gravimetric analysis. [c] M_n(calcd) = MW(TBMA) × conv. + MW(**2**). [d] Determined by SEC.



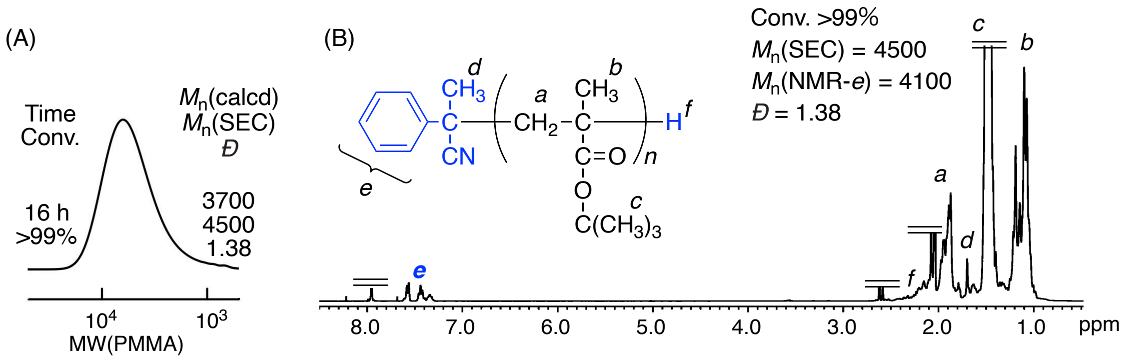
Supplementary Fig. 1. ^{1}NMR spectra (A–D) ($CDCl_3$, 55 °C) of poly(TBMA) obtained by anionic polymerization of TBMA in the presence of various CTAs: $[M]_0/[CTA]_0/[KHMDS]_0/[18\text{-crown-}6]_0$ = 750/30/3.0/3.3 mM in THF at 0 °C.



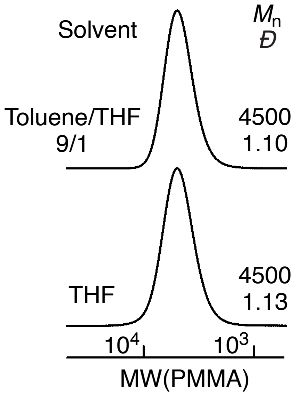
Supplementary Fig. 2. Effect of base catalyst on anionic polymerization of TBMA in the presence of **2**: $[M]_0/[\mathbf{2}]_0/[\text{base catalyst}]_0/[\text{additive}]_0 = 750/30/3.0/3.3$ mM in THF at 0 °C.



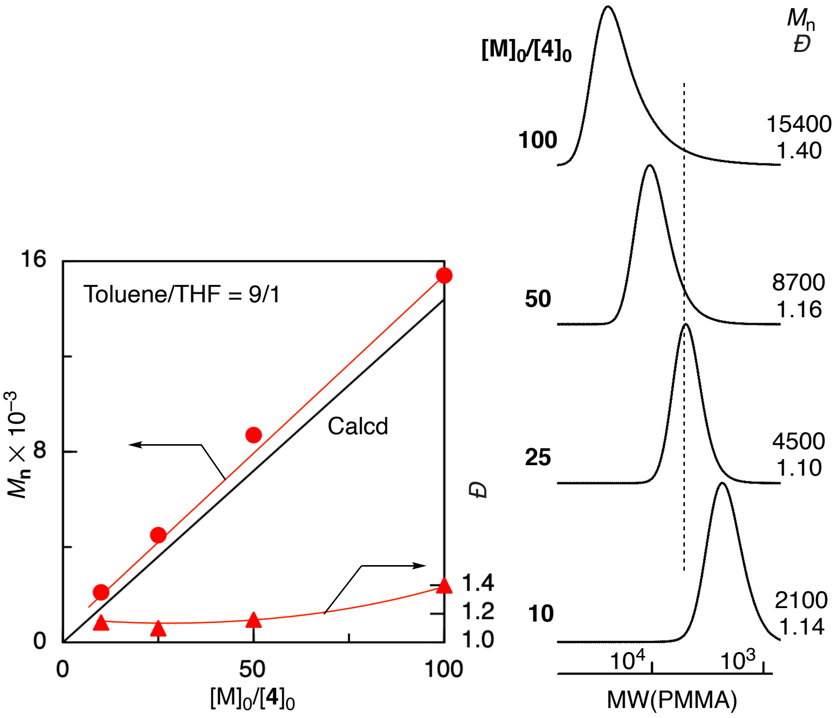
Supplementary Fig. 3. Reversible chain transfer and reversible termination for controlling anionic polymerization.



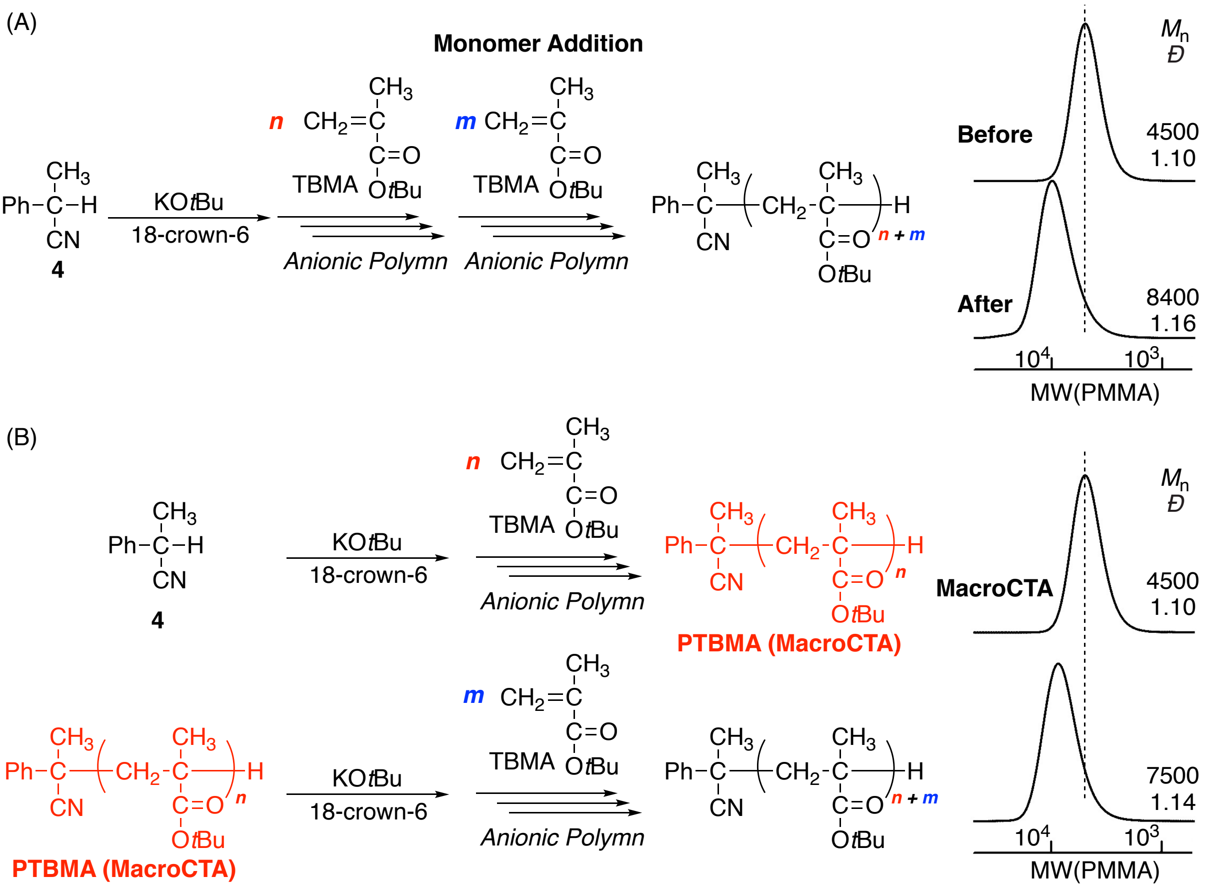
Supplementary Fig. 4. SEC curve (A) and ^{1}H NMR spectrum ($(CD_3)_2CO$, 55 °C) (B) of poly(TBMA) obtained by anionic polymerization of TBMA using KH in the presence of **4**: $[M]_0/[\mathbf{4}]_0/[KH]_0/[18\text{-crown-6}]_0$ = 750/30/3/3.3 mM in THF at 0 °C.



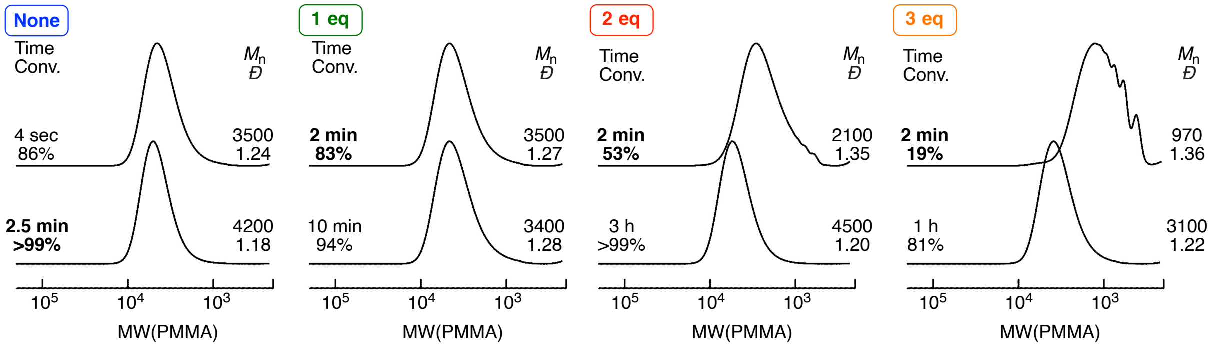
Supplementary Fig. 5. Effect of solvent on anionic polymerization of TBMA using **4**: $[M]_0/[\mathbf{4}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-6}]_0$ = 750/30/3.0/3.3 mM in toluene/THF (9/1 v/v) or THF at 0 °C.



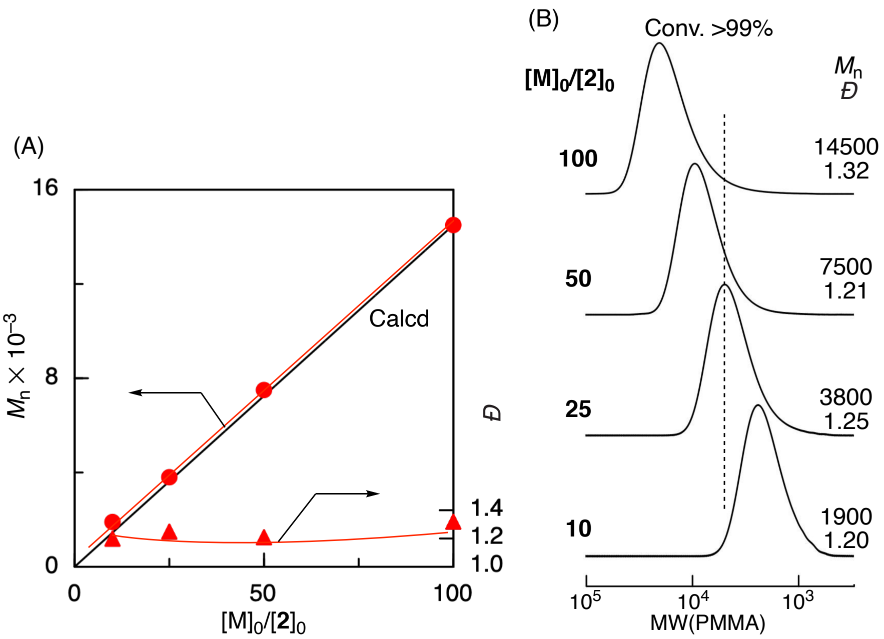
Supplementary Fig. 6. Effect of $[M]_0/[\mathbf{4}]_0$ on anionic polymerization of TBMA: $[M]_0/[\mathbf{4}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-6}]_0$ = 750/30/3.0/3.3 mM in toluene/THF (9/1 v/v) at 0 °C.



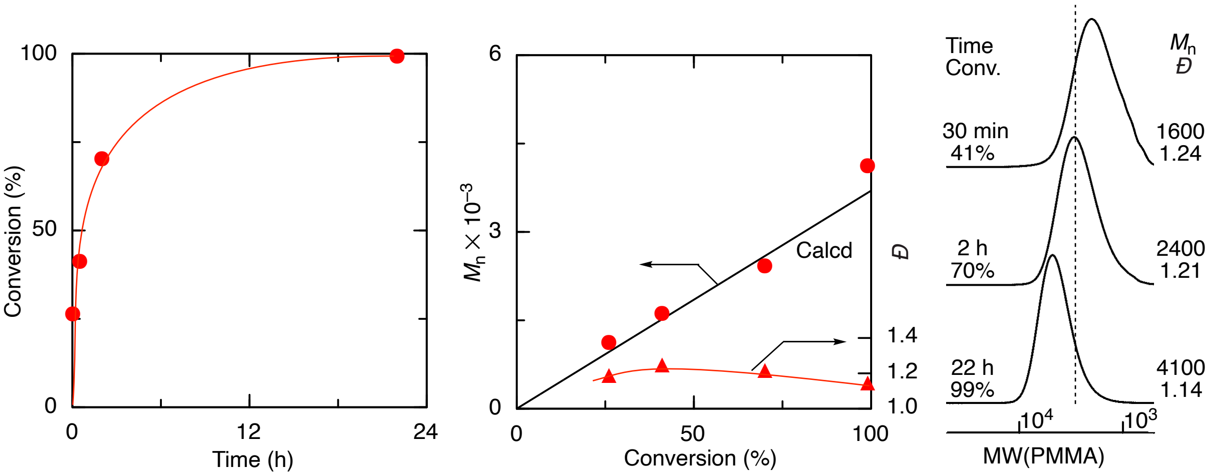
Supplementary Fig. 7. Monomer addition experiment (A) and chain-extension reaction using isolated polymer as macroCTA (B): $[M]_0/[M]_{add}/[\mathbf{4}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-}6]_0$ = 750/750/30/3.0/3.3 mM in THF at 0 °C (A), $[M]_0/[\mathbf{4}]_0$ or $[\text{macroCTA}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-}6]_0$ = 750/30/3.0/3.3 mM in THF at 0 °C (B).



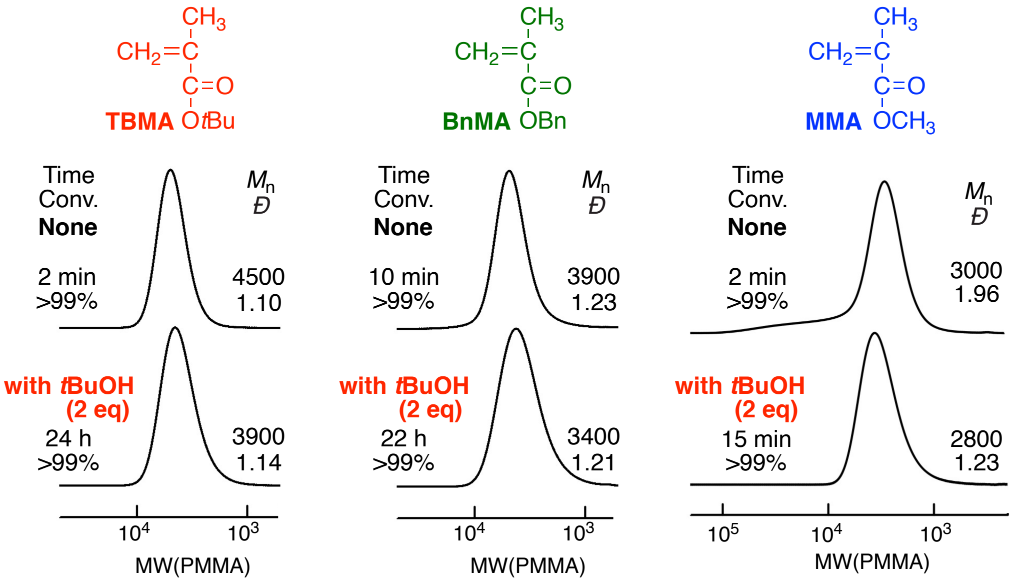
Supplementary Fig. 8. Effect of amounts of *t*BuOH on anionic polymerization of TBMA: $[M]_0/[\mathbf{2}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-}6]_0/[\textit{t}BuOH]$ = 750/30/3.0/3.3/0–9.0 mM in THF at 0 °C.



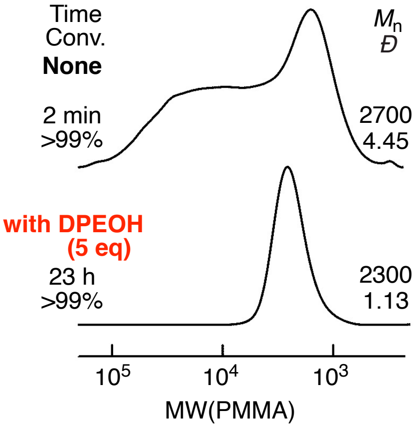
Supplementary Fig. 9. Effect of $[M]_0/[\mathbf{2}]_0$ on anionic polymerization of TBMA in the presence of *t*BuOH: $[M]_0$ = 750 mM, $[M]_0/[\mathbf{2}]_0$ = 10–100, $[\mathbf{2}]_0/[KO{\it t}Bu]_0/[18\text{-crown-6}]_0/[{\it t}BuOH]_0$ = 10/1/1.1/2 in THF at 0 °C.



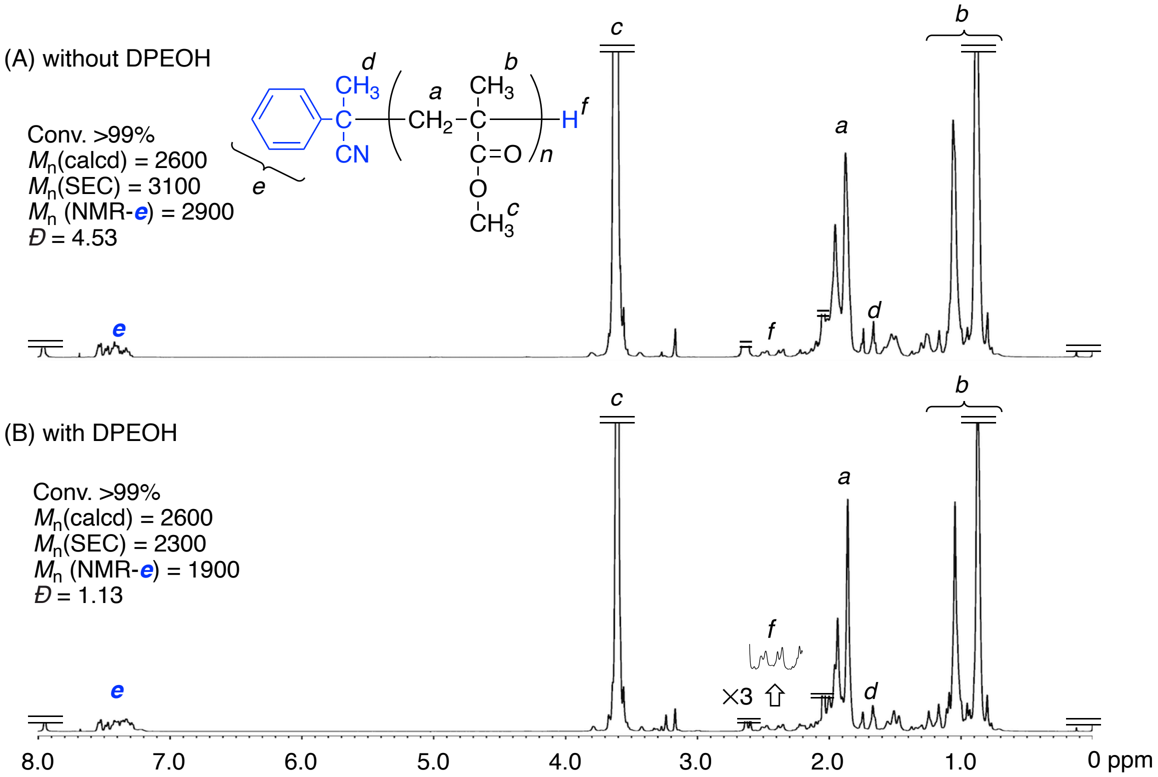
Supplementary Fig. 10. Anionic polymerization of TBMA using as-purchased toluene without purification: $[M]_0/[\mathbf{4}]_0/[KO{\it t}Bu]_0/[18\text{-crown-6}]_0$ = 750/30/3.0/3.3 mM in toluene/THF (9/1 v/v) at 0 °C.



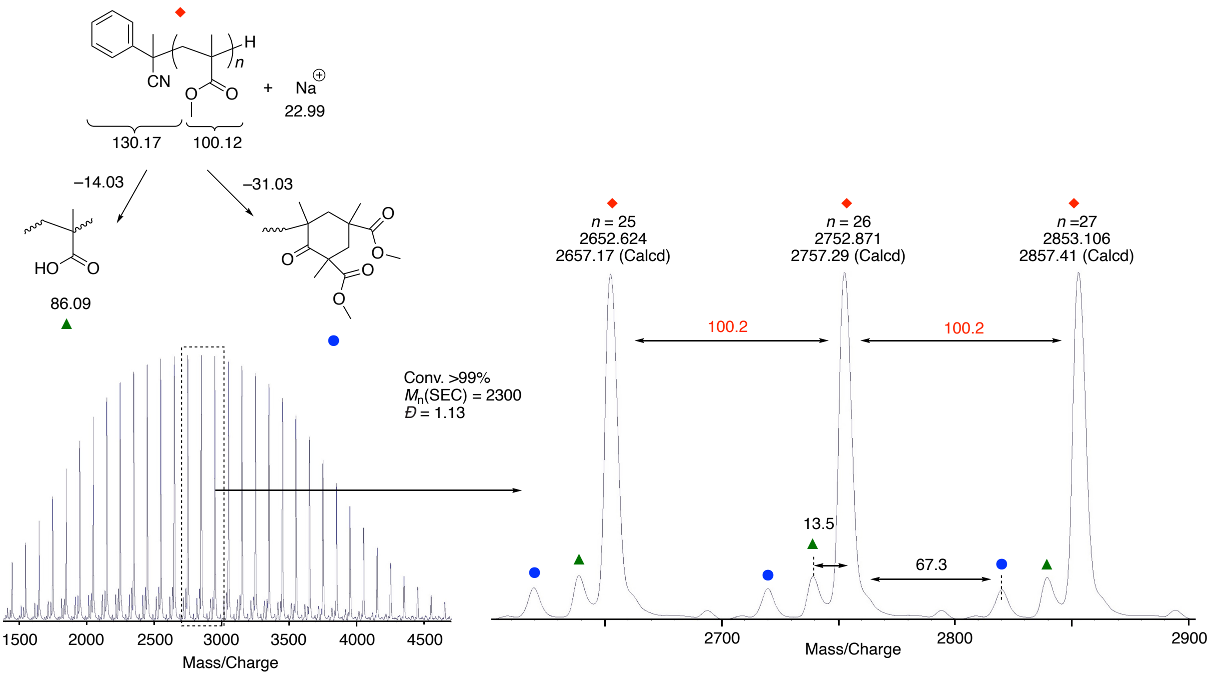
Supplementary Fig. 11. SEC curves of the polymers obtained by anionic polymerization of various methacrylates in the absence or presence of *t*BuOH: $[M]_0/[\mathbf{4}]_0/[KO\textit{t}Bu]_0/[18\text{-crown-}6]_0/[\textit{t}BuOH]_0$ = 750/30/3.0/3.3/0 or 6.0 mM at 0 °C in THF (for TBMA and BnMA) or in toluene/THF (9/1 v/v) (for MMA).



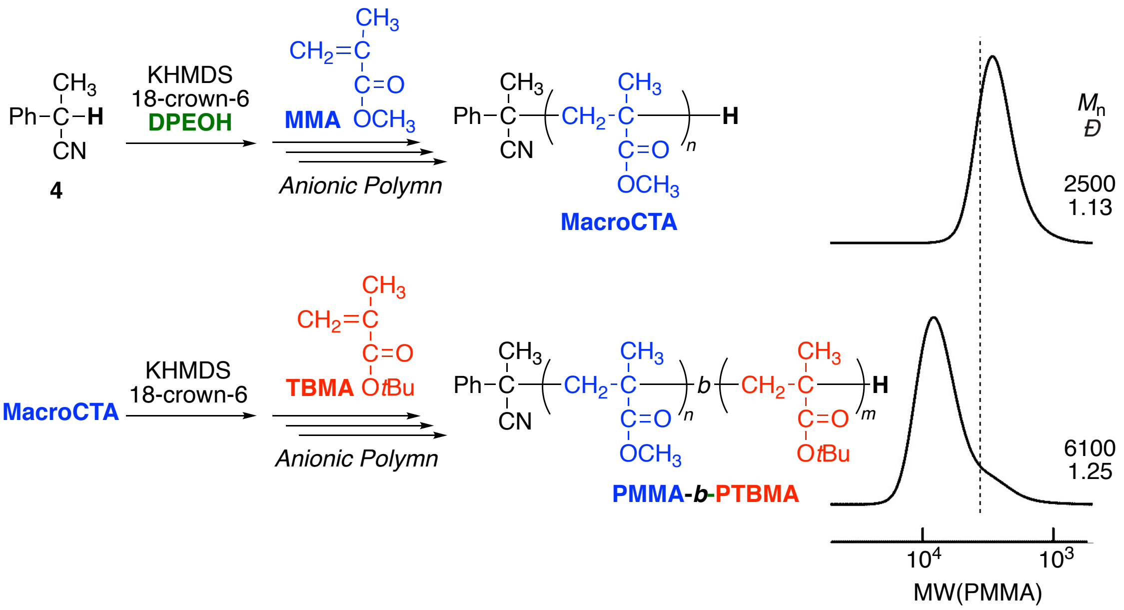
Supplementary Fig. 12. SEC curves of PMMA obtained by anionic polymerization using KHMDS in the absence or presence of DPEOH: $[MMA]_0/[\mathbf{4}]_0/[KHMDS]_0/[18\text{-crown-}6]_0/[DPEOH]_0$ = 750/30/3.0/3.3/0 or 15 mM in toluene/THF (9/1 v/v) at 0 °C.



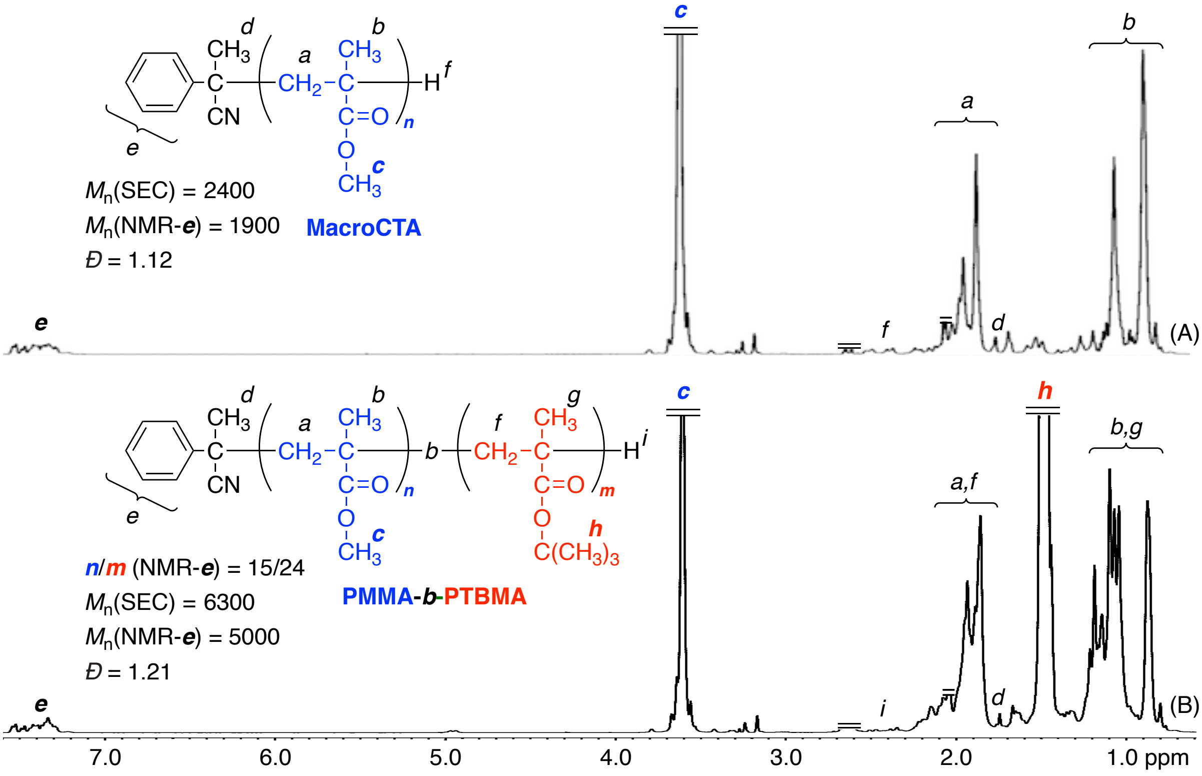
Supplementary Fig. 13. ^{1}H NMR spectra ($(CD_3)_2CO$, 50 °C) of poly(MMA) obtained by anionic polymerization in the absence (A) or presence (B) of DPEOH.



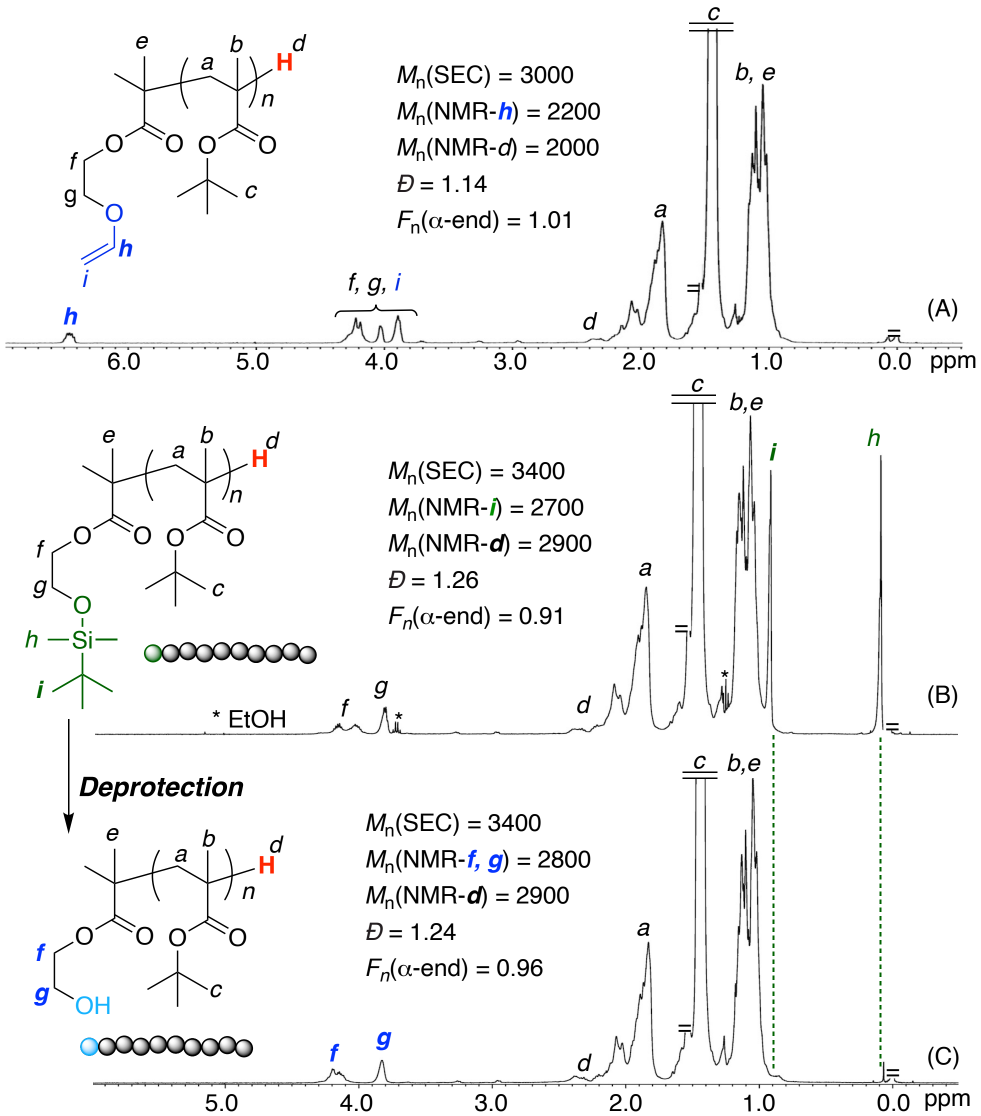
Supplementary Fig. 14. MALDI-TOF-MS spectrum of poly(MMA) obtained by anionic polymerization in the presence of DPEOH.



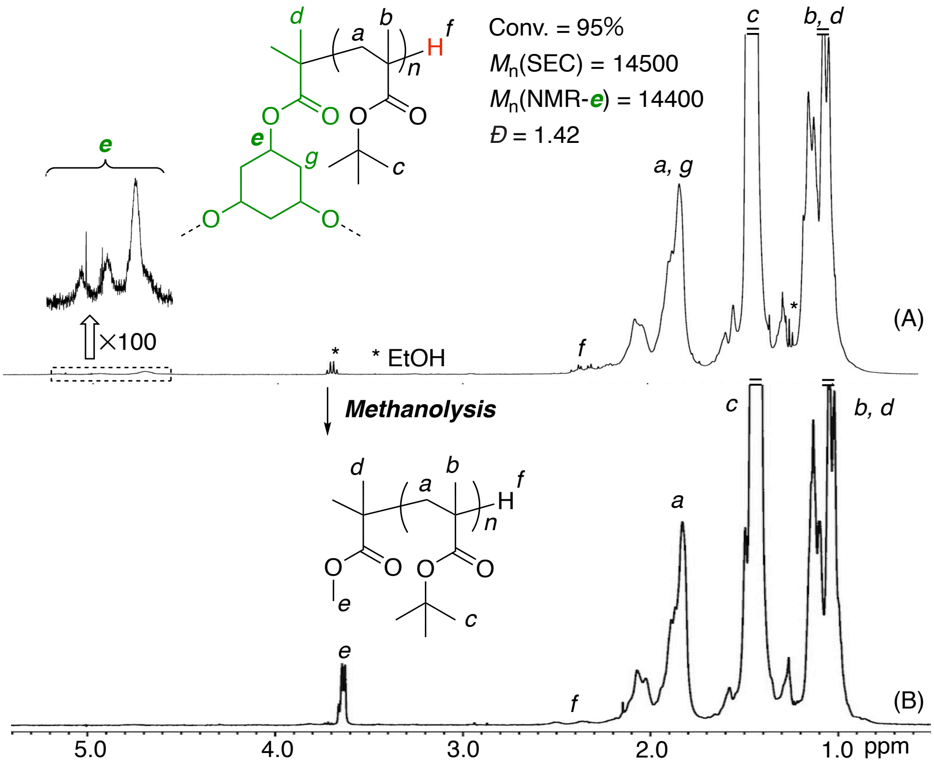
Supplementary Fig. 15. SEC curves of PMMA as macroCTA and poly(MMA-*b*-TBMA) obtained by anionic polymerization: [MMA]$_0$/[**4**]$_0$/[KHMDS]$_0$/[18-crown-6]$_0$/[DPEOH]$_0$ = 750/30/3.0/3.3/6.0 mM in toluene/THF (9/1 v/v) at 0 °C. [TBMA]$_0$/[macroCTA]$_0$/[KHMDS]$_0$/[18-crown-6]$_0$ = 750/30/3.0/3.3/6.0 mM in toluene/THF (9/1 v/v) at 0 °C.



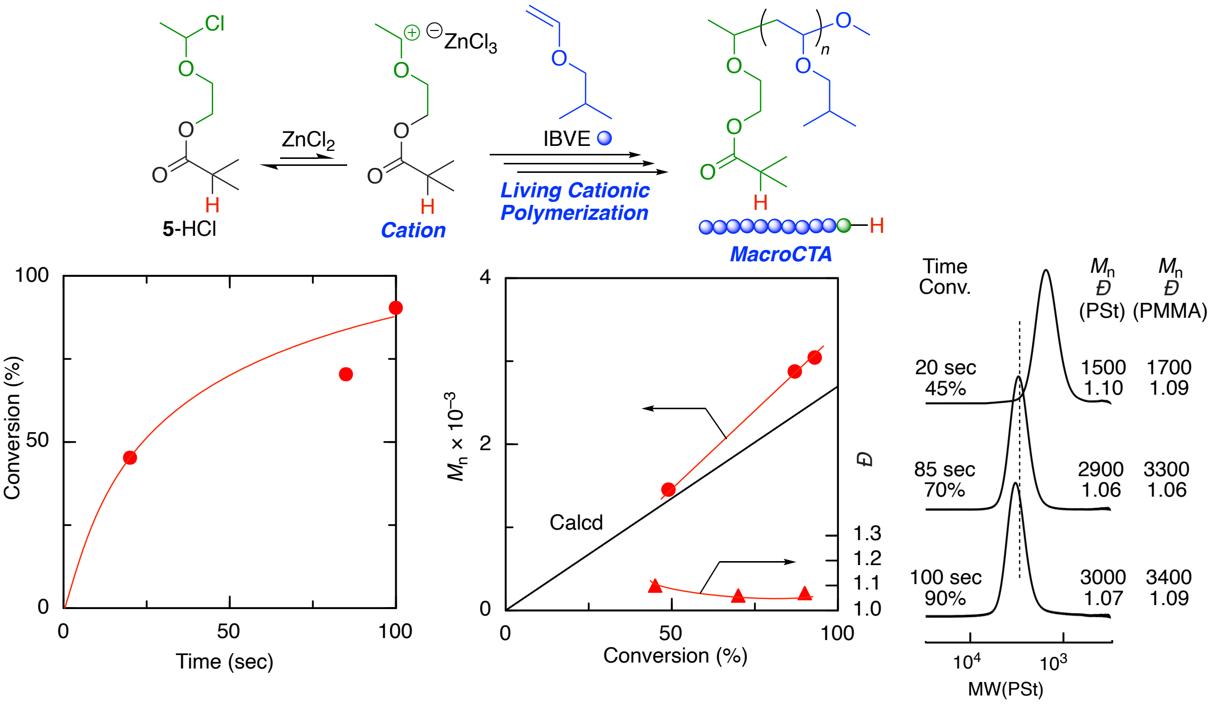
Supplementary Fig. 16. ^{1}H NMR spectra ((CD$_3$)$_2$CO, 50 °C) of poly(MMA) obtained from **4** (A) and poly(MMA-*b*-TBMA) obtained from the PMMA as macroCTA (B).



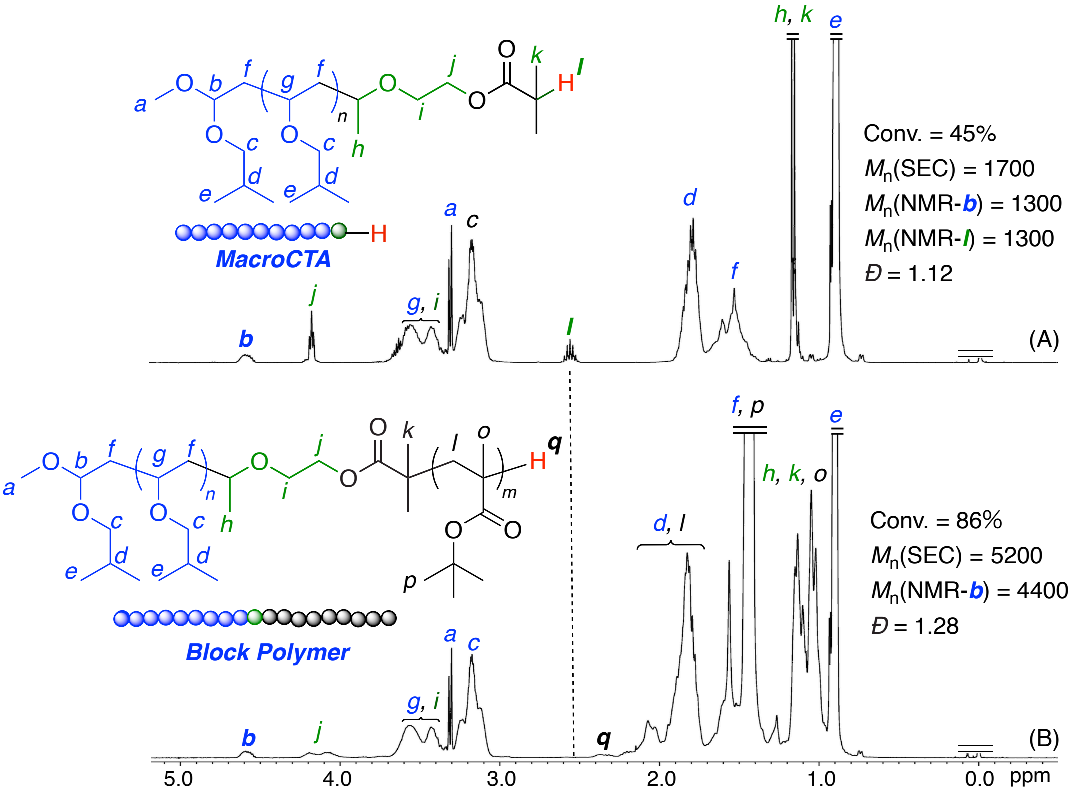
Supplementary Fig. 17. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of end-functionalized poly(TBMA) obtained by anionic polymerization using **5** (A) and **6** (B) and by subsequent deprotection of silyl group (C).



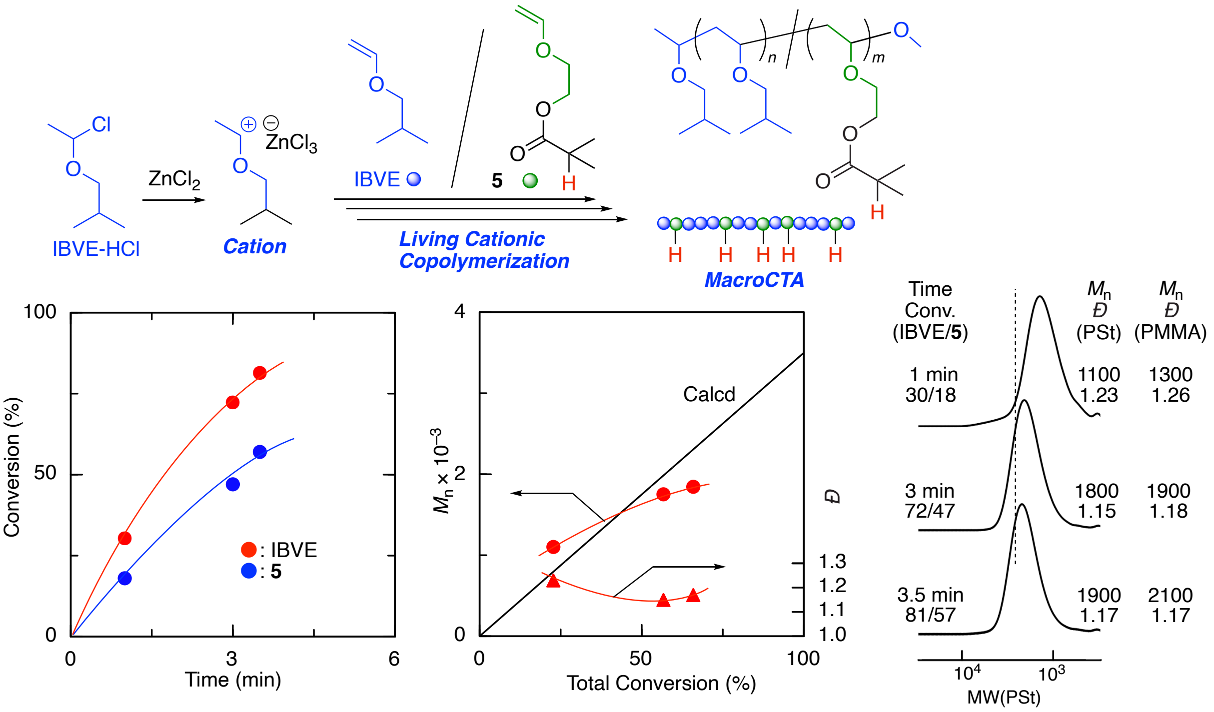
Supplementary Fig. 18. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of star poly(TBMA) obtained by anionic polymerization using **7** (A) and the polymer obtained after methanolysis (B).



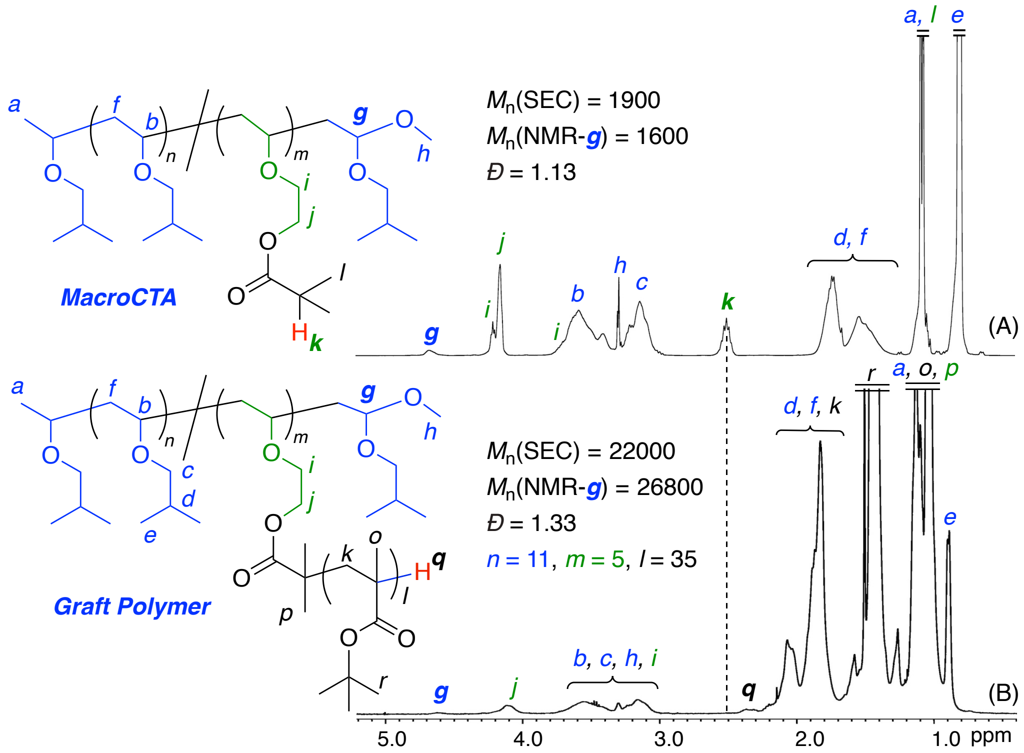
Supplementary Fig. 19. Living cationic polymerization of IBVE using HCl adduct of **5** (**5**-HCl) as an initiator: $[IBVE]_0/[\mathbf{5}\text{-HCl}]_0/[ZnCl_2]_0$ = 500/20/2.0 mM in toluene/Et_2O (9/1 v/v) at 0 °C.



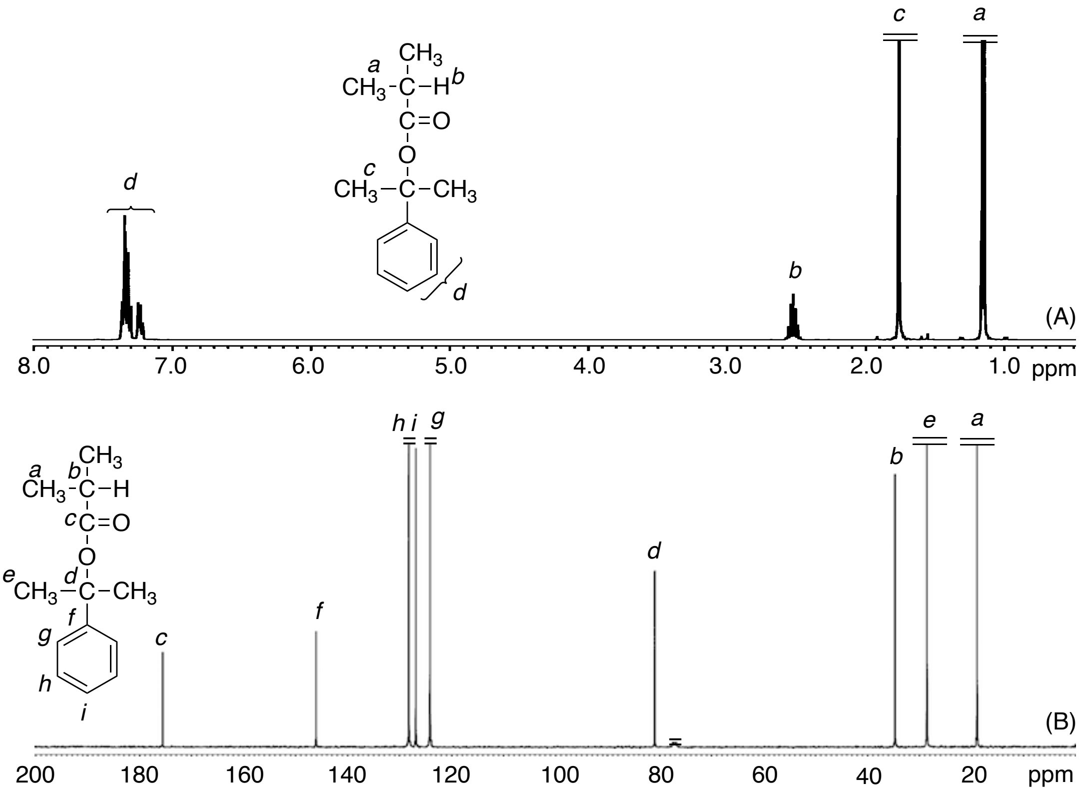
Supplementary Fig. 20. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(IBVE) obtained bu living cationic polymerization of IBVE using **5**-HCl (A) and poly(IBVE-*b*-TBMA) obtained in by anionic polymerization of TBMA using the poly(IBVE) as macroCTA (B).



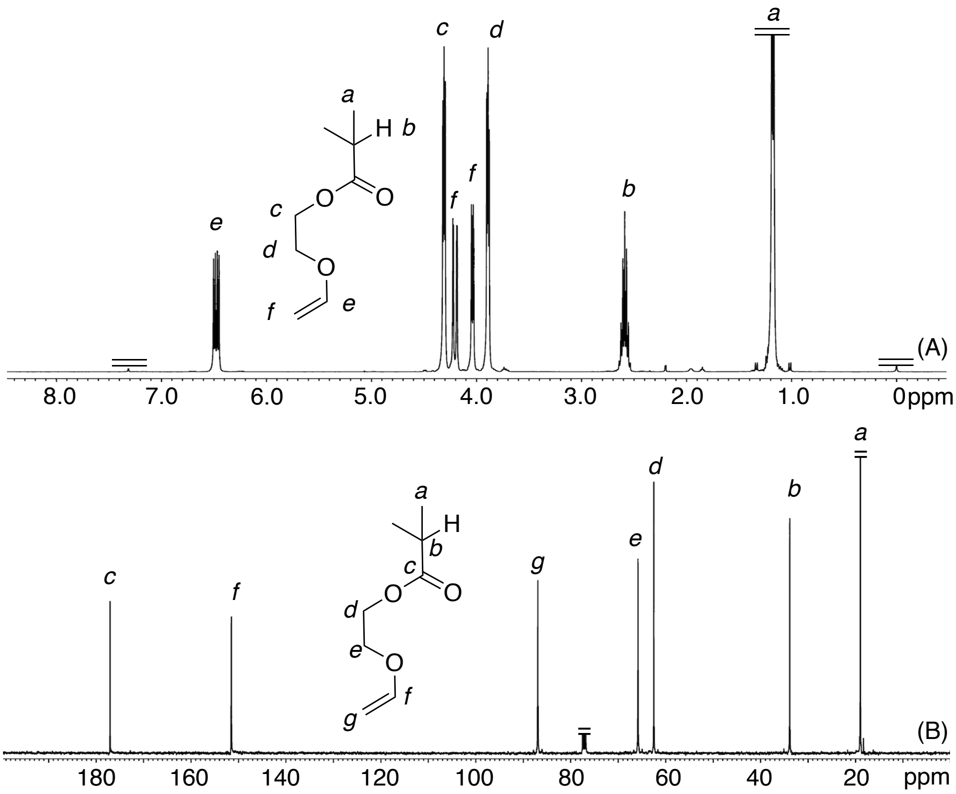
Supplementary Fig. 21. Living cationic copolymerization of IBVE and **5**: [IBVE]$_0$/[**5**]$_0$/[IBVE-HCl]$_0$/[$ZnCl_2$]$_0$ = 260/260/20/2.0 mM in toluene/Et_2O (9/1 v/v) at 0 °C.



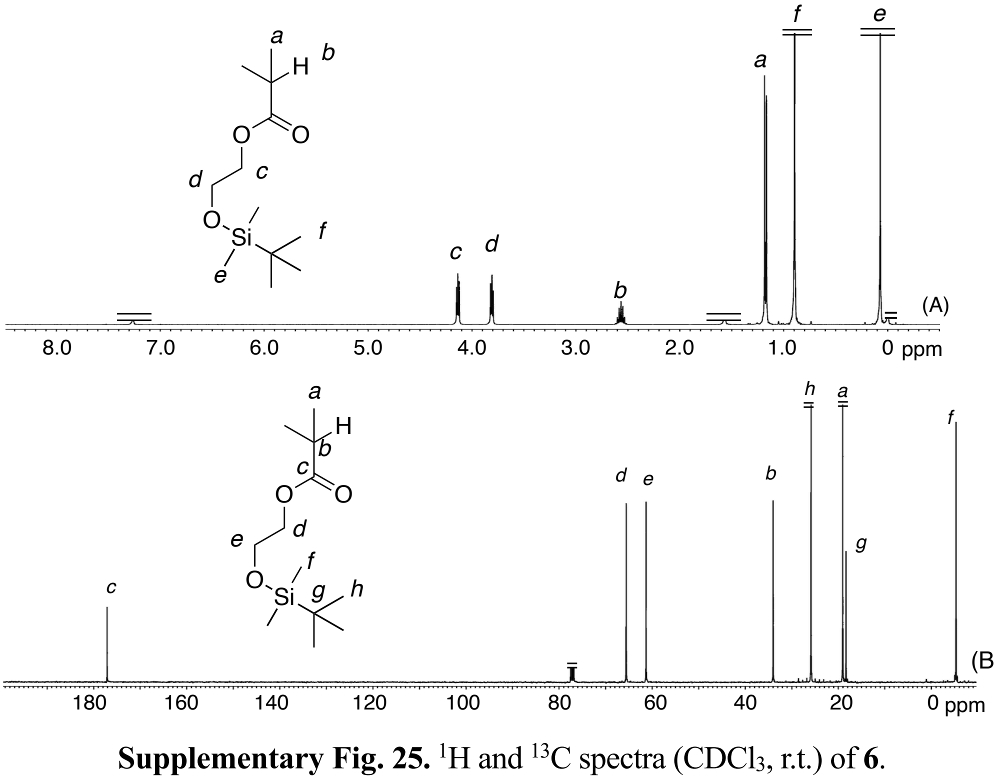
Supplementary Fig. 22. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(IBVE-*co*-**5**) obtained by living cationic copolymerization of IBVE and **5** (A) and poly(IBVE-*g*-TBMA) by anionic polymerization of TBMA using the poly(IBVE-*co*-**5**) as macroCTA (B).



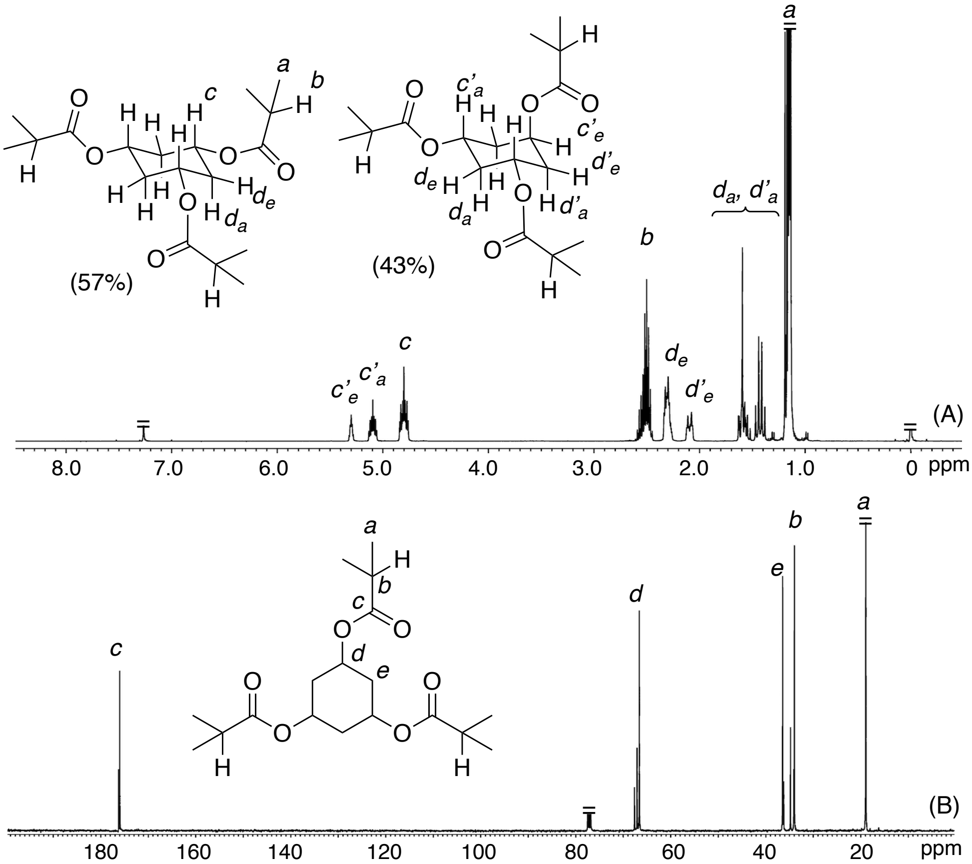
Supplementary Fig. 23. ^{1}H and ^{13}C spectra ($CDCl_3$, r.t.) of **2**.



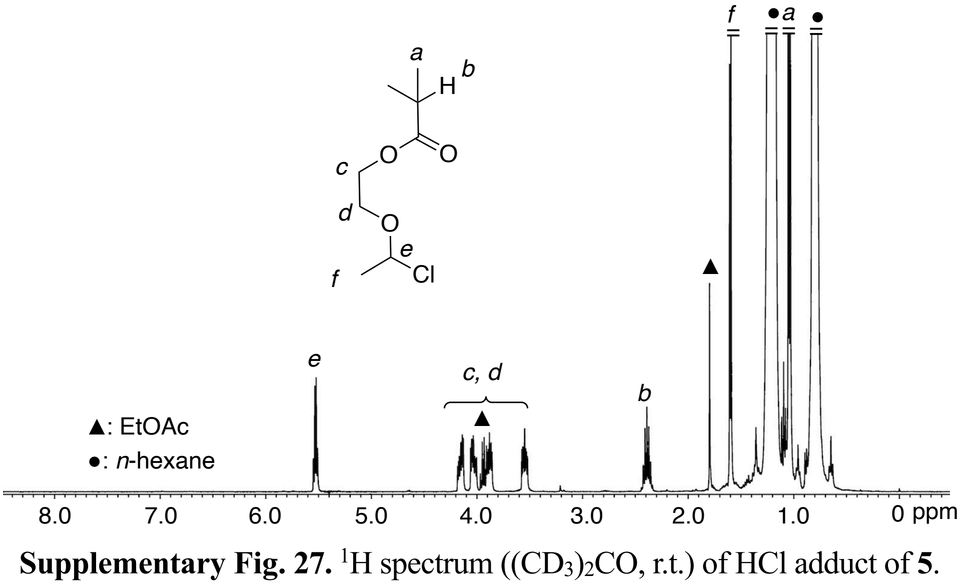
Supplementary Fig. 24. ^{1}H and ^{13}C spectra (CDCl$_3$, r.t.) of **5**.



Supplementary Fig. 25. ^{1}H and ^{13}C spectra (CDCl$_3$, r.t.) of **6**.



Supplementary Fig. 26. ^{1}H and ^{13}C spectra (CDCl$_3$, r.t.) of **7**.



Supplementary Fig. 27. ^{1}H spectrum ((CD$_3$)$_2$CO, r.t.) of HCl adduct of **5**.